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Lithium and potassium aminoalkoxides

Abstract: The structures of the Group 1 metal aminoalkoxides $Li[OCH(CH_2CNMe_2)_2]$ (**1**) and $K[OCH(CH_2CNMe_2)_2]\cdot HOCH(CH_2CNMe_2)_2$ (**2**) have been determined. **1** is a hexameric drum in which two Li_3O_3 rings are joined co-facially, whereas **2** is tetrameric and adopts a K_4O_4 ladder structure, novel for homoleptic potassium alkoxides.

Keywords: aminoalkoxide; lithium; potassium; X-ray.

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Introduction

Group 1 metal alkoxides are key reagents in a variety of synthetic protocols, particularly in conjunction with metal alkyls where they act as superbases (Bradsma and Verkruijsse, 1987; Bradsma, 1990; Lochmann, 2000) and precursors to alkoxy derivatives of less electropositive metals (Bradley et al., 1978; Veith et al., 1998), themselves of central importance in many areas of materials science (Bradley, 1989, 1994). As a consequence, the structures of these Group 1 alkoxides, and particularly the control of their degree of aggregation, have been widely studied. In particular, those of the lightest element (Li) have been analysed in detail (Pauer and Power, 1995), with the number of reports diminishing as the group is descended (Bradley et al., 2001). Lithium alkoxides are known to adopt a minimum of 12 distinct structural types, of which monomers require stabilisation by multidentate ligands, dimers are the most common, trimers are rare, tetramers (cubes) well established (Pauer and Power, 1995), and higher oligomers [hexameric (Pauer and Power, 1995) and octameric (Andrews et al., 2002)] and polymers [e.g., LiOMe (Wheatley, 1960)] more scarce.

Our own interest in the chemistry of metal derivatives of functionalised alkoxides as precursors for the chemical vapor deposition of metal oxide thin films (Hollingsworth et al., 2006, 2008, 2010; Johnson et al., 2008a,b) has given us the opportunity to structurally characterise both lithium and potassium salts of the bis-aminoalkoxide $HOCH(CH_2NMe_2)_2$ [1,3-bis-(dimethylamino)-propan-2-ol; Hbdmap], the results of which are reported herein.

Results and discussion

Compounds **1** and **2** were prepared by deprotonation of Hbdmap by $LiBu^n$ and KH, respectively. Both are air-sensitive solids (particularly **2**) soluble in common organic solvents.

Compound **1** adopts a hexameric structure with two six-membered Li_3O_3 rings fused co-facially via O:→Li coordination (Figure 1) to form a hexagonal drum; this is the same structural motif previously seen for $LiOSiMe_2$(naphthyl) (Bazhenova et al., 1987), $LiOCMe_2Ph$ (Chisholm et al., 1991a), $LiOCMe_2PEt_2$ (Jones et al., 1992), $LiO(CH_2)CMe_3$ (Willard and Carpenter, 1985) and lithium 1-methyl-(*S*)-2-(hydroxymethyl) pyrrolidine (Strohmann et al., 2004). It is, however, in contrast to the octameric structure of the closely related species $[Li(dmae)]_8$ (Hdmae=$HOCH_2CH_2NMe_2$, dimethylaminoethanol), in which the hexagonal drum in **1** is capped along one side by a further $[Li(dmae)]_2$ unit (Andrews et al., 2002). The structure of Li(tdmap) [Htdmap = $HOC(CH_2NMe_2)_3$, 1,3-bis(dimethylamino)-2-(dimethylaminomethyl)-propan-2-ol] has also been reported and is a dimer; however, the structure is influenced by the inclusion of two equivalents of $LiNMe_2$ in the structure (Müller and Schätzle, 2004). Both **1** and Li(dmae) use only one pendant NMe_2 group for coordination to lithium, the second such ligand in **1** remaining free for further elaboration. We thus conclude that it is steric bulk of the ligand that distinguished the degree of oligomerisation in two structures. Around the Li_3O_3 ring, the Li-O bond lengths alternate between short and long [e.g., Li(1)-O(5) 1.905(5), Li(1)-O(4) 1.936(4) Å], implying some degree of covalent vs. coordinate nature, although the data are at the limit of the ±3σ rule; Li-O bonds within the Li_2O_2 rings that link hexagonal faces are generally longer [1.957(4)–1.986(4) Å]. The tetrahedral coordination about lithium

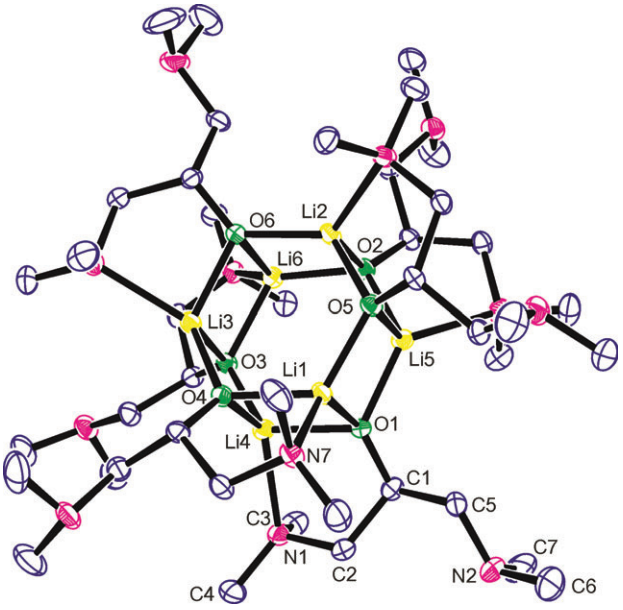
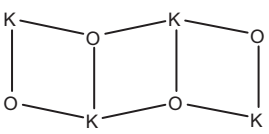


Figure 1 The asymmetric unit of **1** showing the labelling scheme used; thermal ellipsoids are at the 40% probability level. Metrical data around Li(1) and O(1) as representative: Li(1)-O(1) 1.957(4), Li(1)-O(4) 1.936(4), Li(1)-O(5) 1.887(4), Li(1)-N(7) 2.171(5), O(1)-Li(4) 1.945(4), O(1)-Li(5) 1.905(5), O(1)-C(1) 1.389(3), N(1)-Li(4) 2.183(5) Å; O(1)-Li(1)-O(4) 100.07(19), O(6)-Li(1)-O(1) 96.42(18), O(1)-Li(1)-N(7) 128.8(2), O(4)-Li(1)-O(6) 119.9(2), O(4)-Li(1)-N(s7) 86.01(15), O(6)-Li(1)-N(7) 124.4(2), Li(1)-O(1)-C(1) 133.7(2), Li(1)-O(1)-Li(4) 80.11(17), Li(1)-O(1)-Li(5) 84.02(18), Li(4)-O(1)-C(1) 111.12(19), Li(4)-O(1)-Li(5) 114.8(2), C(1)-O(1)-Li(5) 124.61(19) °.

is completed by the N:→Li bond [e.g., Li(1)-N(7) 2.171(5) Å], which is typical of those found in Li(dmae) [2.114(2)–2.189(2) Å] (Andrews et al., 2002) with each bdmap ligand bridging along one rim of the hexagon (rather than spanning between hexagons). The ^{1}H NMR spectrum of **1**, which shows that the CH_2 protons of the ligand are all equivalent, implies a more dynamic structure in solution, with the arms of the bdmap ligand coming on and off within the timescale of the experiment.

The potassium salt **2** crystallises with one molecule of alcohol per alcoholate and is tetrameric, i.e., $[K(bdmap)(Hbdmap)]_4$ (Figure 2). In its ^{1}H NMR spectrum, the signals due to the CH, CH_2 and CH_3 protons show no separation between the alcohol and the alcoholate, but a very broad signal integrating to one hydrogen at *ca*. 11.38 ppm is consistent with the HO group of the coordinated Hbdmap; the ^{13}C NMR spectrum shows no separation for the distinct Hbdmap/bdmap signals. The structure is built around a K_4O_4 ladder, viz:



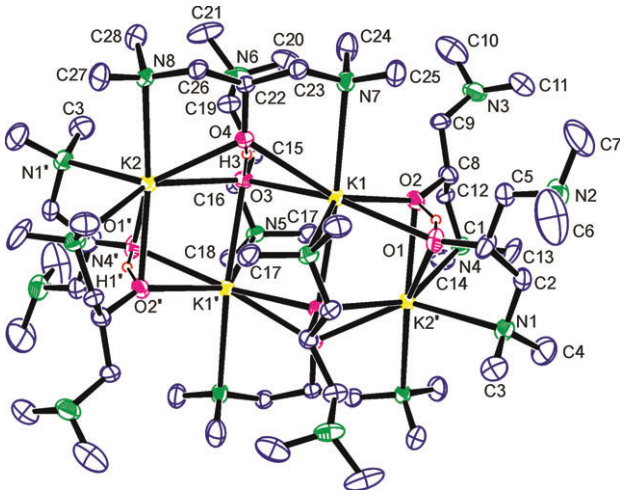


Figure 2 The asymmetric unit of **2** showing the labelling scheme used; thermal ellipsoids are at the 40% probability level. Selected metrical data: K(1)-O(1) 2.770(2), K(1)-O(2) 2.737(2), K(1)-O(3) 2.817(2),K(1)-O(4) 2.857(2), K(1)-O(3′) 2.903(2), K(1)-N(5′) 2.779(3), K(1)-N(7) 3.095(3), K(2)-O(1′) 2.850(3), K(2)-O(2′) 2.686(3), K(2)-O(3) 2.864(2), K(2)-O(4) 2.781(2), K(2)-N(1′) 3.059(3), K(2)-N(4′) 3.110(3), K(2)-N(8) 2.947(3) Å; O(1)-K(1)-O(2) 51.82(8), O(1)-K(1)-O(3) 156.77(8), O(1)-K(1)-O(4) 152.90(8), O(1)-K(1)-O(3′) 76.69(8), O(1)-K(1)-N(5′) 84.46(9), O(1)-K(1)-N(7) 104.16(8), O(2)-K(1)-O(3) 111.34(7), O(2)-K(1)-O(4) 145.19(7), O(2)-K(1)-O(3′) 92.94(7), O(2)-K(1)-N(5′) 134.66(8), O(2)-K(1)-N(7) 100.17(8), O(3)-K(1)-O(4) 50.20(7), O(3)-K(1)-O(3′) 89.76(7), O(3)-K(1)-N(5′)105.93(8), O(3)-K(1)-N(7) 94.10(8), O(4)-K(1)-N(7) 58.82(7), O(4)-K(1)-O(3′) 113.62(7), O(4)-K(1)-N(5′) 79.52(7), O(3′)-K(1)-N(5′) 61.92(7), O(3′)-K(1)-N(7) 163.89(7), N(5′)-K(1)-N(7) 102.01(8), O(1′)-K(2)-O(2′) 51.43(8), O(1′)-K(2)-O(3) 76.08(7), O(1′)-K(2)-O(4) 125.92(7), O(1′)-K(2)-N(1′) 59.85(8), O(1′)-K(2)-N(4′) 101.24(8), O(1′)-K(2)-N(8)152.41(9), O(2′)-K(2)-O(3) 94.92(7), O(2′)-K(2)-O(4)118.23(7), O(2′)-K(2)-N(1′) 97.12(9), O(2′)-K(2)-N(4′) 61.81(7), O(2′)-K(2)-N(8) 153.80(8), O(3)-K(2)-O(4) 50.46(6), O(3)-K(2)-N(1′) 108.63(8), O(3)-K(2)-N(4′) 148.03(8), O(3)-K(2)-N(8) 102.20(7), O(4)-K(2)-N(1′) 138.13(8), O(4)-K(2)-N(4′) 119.01(8), O(4)-K(2)-N(8) 62.16(7), N(1′)-K(2)-N(4′) 96.49(9), N(1′)-K(2)-N(8) 96.02(9), N(4′)-K(2)-N(8) 94.24(8) °. Symmetry operation: -x, -y, -z.

The structure consists of two K(bdmap)·HBdmap units which form a K_2O_2 ring; two rings are linked through an inversion centre. Each potassium in the asymmetric unit is seven-coordinate, although neither adopts the geometry of a regular coordination polyhedron. K(1) has an N_2O_5 ligand set, whereas K(2) is ligated in an N_3O_4 manner. For K(1), the ligands comprise three μ_2-O [O(1, 2, 4)], two μ_3-O [O(3, 3′)] and two N:→K interactions; conversely, for K(2), the ligands are three μ_2-O [O(1′, 2′, 4)], one μ_3-O [O(3)] and three N:→K bonds. For the ligands, two bdmap ligands (one at each end of the ladder) incorporate a μ_2-O and *O,N* chelate one metal, whereas the two bdmap ligands at the heart of the ladder embody a μ_3-O and *O,N* chelate one potassium. The Hbdmap ligands also divide into two bonding modes: the pair at the end of the ladder behave like the bdmap in the same location [μ_2-O

and *O,N* chelation], whereas each of the second pair spans one edge of the ladder in a μ_2-O and *O,N,N* chelating mode. Thus, of the eight Hbdmap/bdmap ligands, six retain one uncoordinated amine function and only two fully utilise their bonding capacity. The two types of ligand are linked by an O-H·O hydrogen bond [O(1)-H(1)...O(2), H(1)...O(2) 1.42(6), O(1)...O(2) 2.407(4) Å, ∠O(1)-H(1)...O(2) 155(5) °; O(3)-H(3)...O(4), H(3)...O(4) 1.34(6), O(3)...O(4) 2.407(3) Å, ∠O(1)-H(1)...O(2) 157(5) °]. The generally strained nature of the bonding makes discerning trends in metrical data difficult, and only broad generalisations can be made. K-O bonds involving the μ_2-O [2.770(2)–2.857(2) Å] are generally shorter than those involving the μ_3-O [2.864(2)–2.903(2) Å], whereas the N:→K are generally long [2.947(3)–3.110(3) Å], save for the chelating nitrogen associated with the μ_3-O(3) which is notably shorter [K(1)-N(5′) 2.779(3) Å]. For comparison, the N:→K bonds in $Li_8K_6(dmae)_{12}O$ are 2.848(5) and 2.850(4) Å (Andrews et al., 2002).

The known structural chemistry of homoleptic potassium alkoxides is limited (Bradley et al., 2001). Although all the reported structures contain K_2O_2 rings, the most common structural variation is the K_4O_4 cubane (Weiss et al., 1970; McGreary et al., 1991; Veith et al., 2010), e.g., $[KOBu^t]_4$ (Weiss et al., 1967); other variations, i.e., polymeric $[KOMe]_\infty$ (Weiss, 1963), dimeric $[KOSiPh_2(OSiPh_2)_2OSiPh_2OH]_2$ (Laermann et al., 1997) and hexameric drum $[KO(CH_2)CMe_3]_6$ (Willard and Carpenter, 1986), are extremely rare. Precedent for alcohol-solvated potassium alkoxides exists in the form of $[KOBu^t{\cdot}HOBu^t]_\infty$, which forms a polymeric structure built up of hydrogen-bonded K_2O_2 rings (Chisholm et al., 1991b). The structure of **2** is thus a new variation for this class of alkoxide.

In contrast to the ^{1}H NMR spectrum of **1**, that of **2** shows the methylene protons $[CH_aH_b]$ are non-equivalent by virtue of the locked arrangement of the ligand bridging two potassium centres. However, there are no separate signals for the free, non-coordinated arm of one bdmap ligand, suggesting some degree of structural non-rigidity in solution, nor does the spectrum differentiate the protonated and non-protonated alkoxides present.

In addition to these comments on the relationship of **1** and **2** to specific analogues, it is worth noting that both structures conform to the "ring-laddering/ring stacking" principles first enunciated in the seminal work of Snaith and Mulvey on lithium amides (Gregory et al., 1991; Mulvey, 1991) and, subsequently, on intermetallic Group 1 amides (Mulvey, 1998) and later developed to include lithium heterocarboxylates (Downard and Chivers, 2001); similar structural principles also apply to lithium enolates (Seebach, 1988). Thus, **1** can be described either as a ladder of three $[Li_2O_2]$ dimers which cyclise head-to-tail or as two six-membered $[Li_3O_3]$ trimers which associate face-to-face. Similarly, **2** is a ladder in which two $[K_2O_2]$ dimers join to form a linear array of three fused K_2O_2 rings.

Experimental

General procedures

All operations were performed under an atmosphere of dry argon using standard Schlenk line and glovebox techniques. Hexanes and toluene solvents were dried using a commercially available solvent purification system (Innovative Technology Inc. MA, USA) and degassed under argon prior to use. Deuterated benzene (C_6D_6) NMR solvent was purchased from Fluorochem Hadfield, UK and dried by refluxing over potassium before isolating via vacuum distillation. All dry solvents were stored under argon in Young's ampoules over 4-Å molecular sieves. 1,3-Bis(dimethylamino)-2-propanol (Hbdmap) was dried and purified by distillation prior to use. Solution ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a Brüker Avance 300 spectrometer, whereas ^{7}Li NMR spectra were recorded using a Brüker Avance 500 spectrometer Brüker Coventry, UK. All spectra were obtained at ambient temperature (25°C). ^{1}H and ^{13}C NMR chemical shifts are given in parts per million and referenced internally to residual non-deuterated solvent resonances. The following abbreviations are used: s (singlet), d (doublet), qi (quintet), dd (doublet of doublets), tt (triplet of triplets) and br (broad).

Synthesis of $Li[OCH(CH_2NMe_2)_2]$ (**1**): A stirred solution of $HOCH(CH_2NMe_2)_2$ (Hbdmap) (0.65 ml, 4 mmol) in 20 ml of hexanes was slowly treated at -78°C with a 2.5-M solution of ^{n}BuLi in hexanes (1.6 ml, 4 mmol). The solution was allowed to warm to ambient temperature and refluxed for 24 h, before the volume was reduced *in vacuo*. Crystallisation from the reaction solution at -28°C afforded the product as colourless crystals. Yield: 0.340 g, 56%, m.p 216–219°C. Analysis, found (calc. for $C_7H_{17}LiN_2O$): C 55.1 (55.3), H 11.2 (11.3), N 18.3 (18.4)%. ^{1}H NMR (300 MHz, C_6D_6): 4.12 (qi, 1H, C*H*O, $^3J_{CH_2CHO}$ 6.7), 2.41 (d, 4H, CH_2CHO, $^3J_{CH_2CHO}$ 6.7), 2.33 (s, 12H, NCH_3). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): 71.3 (s, CH_2CHO), 67.1 (s, *C*HO), 46.5 (s, NCH_3). ^{7}Li NMR (194.37 MHz, C_6D_6): 0.21 (s).

Synthesis of $K[OCH(CH_2NMe_2)_2]{\cdot}HOCH_2CH_2NMe_2$ (2). $HOCH(CH_2NMe_2)_2$ (Hbdmap) (3.26 ml, 20 mmol) was added dropwise to a stirred toluene (20 ml) solution of KH (0.401 g, 10 mmol) and the mixture refluxed for 24 h. The toluene was then removed under reduced pressure to yield a golden oil. Crystallisation from the crude oil at ambient temperature afforded the product as yellow, highly air-sensitive crystals. Yield: 2.618 g, 79%, m.p 38–40°C. Analysis, found (calc. for $C_{14}H_{35}KN_4O_2$): C 50.7 (50.9), H 10.5 (10.7), N 16.8 (17.0)%. ^{1}H NMR (300 MHz, C_6D_6): 11.38 (br s, 1H, OH), 4.04 (tt, 2H, C*H*O, $^3J_{CHAHBCHO}$=7.6, $^3J_{CHAHBCHO}$=4.7), 2.46 (dd, 4H, CH_AH$_B$CHO, $^2J_{CHAHB}$=11.9, $^3J_{CHAHBCHO}$=7.6), 2.35 (dd, 4H, CH$_A$$H_B$CHO, $^2J_{CHAHB}$=11.9, $^3J_{CHAHBCHO}$=4.7), 2.27 (s, 24H, NMe_2). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): 68.4 (NCH_2), 65.8 (OCH), 46.6 (NMe_2).

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in Table 1. For all structures, data

Identification code	1	2
Empirical formula	$C_{42}H_{102}Li_6N_{12}O_6$	$C_{56}H_{140}K_4N_{16}O_8$
Formula weight	913.00	1322.24
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	13.5960(3)	10.5939(3)
b (Å)	13.6010(3)	13.9462(6)
c (Å)	20.1660(4)	16.4628(9)
α	90.779(1)	98.2662(15)
β	105.360(1)	108.4821(16)
γ	120.111(1)	111.613(3)
V (Å^3)	3062.29(11)	2048.89(15)
Z	2	1
ρ_{calc} (Mg/Mgm^{-3})	0.990	1.072
μ(Mo-K$_\alpha$) (mm^{-1})	0.065	0.269
F(000)	1008	728
Crystal size (mm)	0.40×0.30×0.30	0.20×0.20×0.15
Theta range for data collection (°)	3.52 to 25.03	5.47 to 25.18.
Reflections collected	53,773	12,130
Independent reflections [R(int)]	53773 [0.0000]	6730 [0.0716]
Reflections observed (>2σ)	39,994	4533
Data completeness	0.993	0.913
Transmission factors (max., min.)		0.9608, 0.9482
Goodness-of-fit on F^2	1.099	1.092
Final R_1, wR_2 indices [I>2σ(I)]	0.1219, 0.3617	0.0628, 0.1256
Final R_1, wR_2 (all data)	0.1491, 0.3748	0.1072, 0.1470
Largest diffraction peak, hole (eÅ^3)	0.548, -0.442	0.250, -0.225

Table 1 Crystal data and structure refinement for compounds **1** and **2**.

were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-K$_\alpha$ radiation (λ=0.71073 Å). Structure solution followed by full-matrix least squares refinement was performed using the WinGX-1.70 (University of Glasgow, Scotland) suite of programmes (Farrugia, 1999). Corrections for absorption (multi-scan) were made in the case of **2**. For **1**, a pseudo-merhohedral twin law to account for 30% twinning (180.0° rotation about -1. 1. 0. direct lattice direction) was included in the refinement model for this structure. Although the R factors remain somewhat higher than desirable, the structure has converged well and is completely unambiguous. Data were truncated to a max Bragg angle of 25° because of intensity drop-off at higher resolution. For **2**, the asymmetric unit consists of half a tetranuclear complex which is located around a centre of inversion at the mid-point of the central K_2O_2 ring. Two out of the four ligands are disordered over two sites in the ratio 65:35. The OH hydrogen atoms have been located in the difference Fourier map and were freely refined.

Supporting information

Crystallographic data for the structural analysis (in CIF format) have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 897223 and 897224 for 2 and 1, respectively. Copies of this information may be obtained from the director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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